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<b>(71) Applicant (for all designated States except US):</b> ELISHA TECHNOLOGIES CO. L.L.C. [US/US]; 2000 US Highway 63 South, Moberly, MO 65270 (US).			
<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> HEIMANN, Robert, L. [US/US]; 1 Circle Drive, Moberly, MO 65270 (US). MCGOWAN, Nancy, M. [US/US]; 19001 Old US Highway 63 North, Sturgeon, MO 65284 (US). DALTON, William, M. [US/US]; 527 W. Carpenter Street, Moberly, MO 65270 (US).			
<b>(74) Agent:</b> BOYER, Michael, Kevin; Orscheln Management Co., 2000 US Highway 63 South, Moberly, MO 65270 (US).			<b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CORROSION RESISTANT LUBRICANTS, GREASES AND GELS			
<b>(57) Abstract</b> <p>The disclosure relates to improved gel/grease compositions as well as grease compositions capable of imparting improved corrosion resistance. The grease includes a silica/silicate mixture that can impart a relatively high pH and corrosion resistant properties to the grease.</p>			

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## TITLE

5 "CORROSION RESISTANT LUBRICANTS, GREASES, AND GELS "

The subject matter herein claims benefit under 35 U.S.C. 111(a), 35 U.S.C. 119(e) and 35 U.S.C. 120 of Provisional Patent Application Serial No. 60/045,466, filed on May 2, 1997; and U.S. Provisional Patent Application Serial No. 60/036,026, filed  
10 on January 31, 1997; both of which are entitled "Corrosion Resistant Lubricants, Greases, and Gels". The disclosure of the aforementioned Provisional Patent Applications is hereby incorporated by reference.

## FIELD OF THE INVENTION

15 The instant invention relates to improved grease compositions as well as grease compositions capable of imparting improved corrosion resistance.

## BACKGROUND OF THE INVENTION

The American Society for Testing and Materials (ASTM D288 standard  
20 definition of the terms relating to petroleum) defines a lubricating grease as a solid to semi-fluid product of dispersion comprising a thickening agent and a liquid lubricant. Other ingredients imparting special properties may be included. This definition indicates that a grease is a liquid lubricant thickened in order to provide properties that are not provided solely by the liquid lubricant. Typically, greases are employed in  
25 dynamic rather than static applications. Gels are normally classified as a colloid and provide utility in non-dynamic applications ranging from sol-gels to cosmetic applications.

Conventional grease formulations are described in "Synthetic Lubricants and High-Performance Functional Fluids", edited by Ronald L. Shubkin (dated 1993). The  
30 characteristics of soap based greases, additives and methods for making conventional greases are described in "The Chemistry of Soap Base Greases" by Glen Brunette, "Additives For Grease", by Dr. Miles Hutchings and "Grease Manufacture in Conventional Kettles" by K.F. Montgomery all of which were presented at the 63rd NLGI Annual Meeting, October 1996. The disclosure of the previously identified  
35 publications is hereby incorporated by reference.

Commercial industrial practice employs lubricating films and greases to prevent galling and fretting. The increased efficiency and complexity of modern machines often require such films and greases to perform under severe operating and environmental conditions. While the composition of a gel may be similar to a grease,  
40 typically gels are employed to solve non-lubricating problems. There is a need in this art for lubricants, greases and gels that also impart corrosion resistance.

## SUMMARY OF THE INVENTION

The instant invention solves problems associated with conventional lubricants and greases by providing an improved composition which imparts corrosion and microbial resistance, and a high dropping point. By "dropping point" it is intended to mean the temperature at which lubricating compositions become fluid and thereby able to drip through an orifice in accordance with ASTM D2265. The inventive grease typically has a minimum dropping point of about 250° C.

The instant invention also provides a composition that can offer an alternative to conventional greases and gels thereby also avoiding the environmental and manufacturing problems associated with conventional grease products. The inventive greases and gels can be tailored to range from microbial resistant to biodegradable; but in either case the greases/gels are non-toxic. While the instant invention is compatible with a wide range of metals and metallic coatings, the instant invention can also obviate the usage of environmentally undesired metals, e.g., chrome, that are conventionally employed for imparting corrosion resistance. Similarly, while the instant invention can be employed with a solvent, in certain aspects the inventive grease/gel can be substantially solvent free. By "substantially solvent free", it is meant that the grease/gel contains less than about 30 wt.%; and normally less than 10 wt.%, of volatile organic compounds (otherwise known as V.O.C.s).

The inventive grease/gel can be employed as a substitute for conventional greases/gels; especially in environments where improved corrosion resistance is desired, e.g., wire rope and strand that is used in a wide range of applications including automotive and marine end-uses. Further, the inventive grease/gel can be employed for reducing, if not eliminating, corrosion under insulation (CUI). That is, corrosion upon metallic surfaces which are covered by an insulating covering or layer, e.g., a mechanically attached insulating sleeve upon a pipe. CUI is particularly problematic in the petroleum industry wherein corrosion can occur under refinery pipes, cracking columns, oil/gas pipelines, reaction vessels, among other areas. Corrosion under insulation can also occur in heating ventilation and cooling (HVAC) water lines, steam lines for chemical processing and power generation, conduits/piping on ships, among other areas. The instant invention can also offer an alternative to silicone containing lubricants. For example, in automotive painting environments silicone oils have been associated with adverse affects, e.g., on the quality of painted surfaces due to low molecular fractions of the silicone-becoming air-borne under ambient conditions. The instant invention, however, can improve the corrosion resistance of silicone containing lubricants and gels.

The fluid or liquid portion of the inventive grease/gel can comprise a base oil comprising at least one member selected from the group consisting of mineral oil, synthetic oil, vegetable oil, fish oil, animal oil among any suitable fluid having lubricating properties. Examples of suitable base oils include at least one member from

the group consisting of animal, vegetable, petroleum derived and synthetic oils such as polyalphaolefin (PAO), silicone oil, phosphate esters, fluorinated oils such as KRYTOX (supplied by the DuPont Company, Wilmington, Delaware), mixtures thereof, among others. Typically, the base oil will comprise about 45 to about 90 wt.% of the grease e.g., about 70 wt. % to about 90 wt. %.

Environmentally preferred lubricants (EPL's) are preferred as base oils in applications where loss of material to the environment can occur. EPL's have the distinction of being biodegradable and/or essentially non-toxic. Biodegradable base oils include, but are not limited to fish oils, vegetable oils, lanolin, synthetic esters, low molecular weight polyalphaolefins, and polyalkylene glycols. Essentially non-toxic base oils include but are not limited to polyalphaolefins, polybutenes, vegetable oils and also lanolins.

For applications requiring that the grease be exposed to a relatively high or low temperature, or wide variation in temperature during operation, synthetic fluids are typically employed, e.g., a diester oil based grease. If the grease comprises a metallic soap grease, then complexing agents can be employed for improving the so-called "dropping point" of the grease. Such agents are usually present in an amount from about 5 to about 25 wt.% of the grease.

A thickener is combined with a base oil to form a grease or gel. The thickener component of the grease can comprise any material that in combination with the selected base oil will produce a semi-fluid or solid structure. Examples of a suitable thickener comprise at least one member selected from the group consisting of soaps of aluminum, lithium, barium, sodium, calcium, mixtures thereof, and, in some cases, silicas and clays, mixtures thereof, among others. Characterization of grease as a function of the thickener is described in greater detail by J. George Wills in "Lubrication Fundamentals" (1980); hereby incorporated by reference. Thickeners of differing composition can be blended together, e.g., TEFLON fluoropolymers and polyethylene, provided they are compatible with one another and with the base oil. Additional ingredients can be combined with the thickener to impart special features or properties such as coupling agents dyes, pigments, anti-oxidants, among other components for tailoring the properties of the grease. Normally, the thickener will comprise about 5 to about 10 wt. % of the grease, and additional ingredients will comprise a total amount of about 5 to about 30 wt.%. However, when thermoplastic powders, for example, polytetrafluoroethylene, polyethylene and the like, are used as thickeners can be used effectively in amounts up to about 50% by weight.

The inventive grease can also comprise at least one anti-wear agent which may also function as a pour-point depressant, and/or an extreme pressure agent. Examples of suitable anti-wear agents comprise at least one member from the group consisting of tricresyl phosphate, dithiophosphates, fatty acid esters, metal stearates, zinc oxide, borax, boron nitride, ammonium molybdate, calcium carbonate, mixtures thereof, among others. In some cases, molybdenum disulfide, polyethylene,

polytetrafluoroethylene, polyvinylidene fluoride/polyvinyl fluoride and dispersions thereof; mixtures thereof, among others, can be added to reduce friction and wear.

Anti-wear agents can comprise about 0.1 to about 2 wt.% of the grease. Examples of extreme pressure agents can comprise at least one member selected from the group of graphite, triphenyl phosphorothionate, chlorinated paraffins, dithiocarbonates, fatty oils, fatty acids, or fatty acid esters with a phosphite adduct; sulfurized fatty oils, fatty acids, or fatty acid esters; molybdenum disulfide, tungsten disulfide, phosphate esters, phosphorous-sulfur containing compounds, mixtures thereof, among others. Powdered extreme pressure agents can protect rough or uneven surfaces as well as tapered crevices when the agents are composed of a sufficiently wide particle size distribution and with an appropriate limit on the maximum particle size. The particle size distribution would normally allow the EP agent to fill in gaps and spaces upon the article to be protected (such as exist in wire rope, stranded cable, or armored cable). Extreme pressure agents can comprise about 2 to about 10 wt.% of the grease.

Surfactants, wetting agents, or surface active agents can optionally be included when desirable, such as pine oil and derivatives, Tall oil and derivatives, ethoxylates, acetylenic diols, silicones, silanes, sulfonates, fluorosurfactants, mixtures thereof, among others.

The inventive grease can further comprises at least one of silica and/or a silicate containing component for imparting corrosion resistance, e.g., a component containing -SiO- groups. The silicate containing component can interact with another component of the grease and/or a surface being protected. The interaction can provide a protective surface having enhanced corrosion resistance. The amount of silica/silicate containing material can range from about 1 to about 50 wt.% of the grease. The specific amount of silicate containing material is ascertained when considering the relative importance of corrosion resistance and lubrication for a particular application as well as the thickening ability of the silica or silicate.

In some cases, it is desirable to utilize a gel with less potential for oil to migrate out of or separate from the gel. Drying oils, e.g., linseed, or non-drying polymers can be added to the gel to reduce oil loss or migration from the gel. Polymers include but are not limited to polyurethane, silicone, acrylic, epoxy and oil modified polymers. High solids polymers or substantially solvent free polymers are environmentally preferred, e.g., polymers containing less than about 30 wt.% V.O.Cs.

In other cases, it is desirable for the gel to form an outer self-supporting layer or skin. The portion of the gel underlying the self-supporting layer normally remains in a substantially unchanged state, e.g., the retained physical characteristics of the underlying portion resemble those of an newly applied gel coating. An added benefit of forming a self-supporting layer or so-called skin at the surface of the gel which provides improved resistance to rainwater and incidental contact.

## CROSS REFERENCE TO RELATED PATENTS AND PATENT APPLICATIONS

5 The subject matter of the instant invention is related to copending and commonly assigned Non-Provisional U.S. Patent Application Serial No. \_\_\_\_\_ (Attorney Docket No. EL001RH-8), filed on even date herewith; Serial Nos. 08/850,323 and 08/850,586 (EL001RH-6 and EL001RH-7 filed on May 2, 1997); Serial No. 08/791,336 (Attorney Docket No. EL001RH-5 filed on January 31, 1997) and 08/791,337 (Attorney Docket No. EL001RH-4 filed on January 31, 1997) in the names of Robert L. Heimann et al.,  
10 as a continuation in part of Serial No. 08/634,215 (Attorney Docket No. EL001RH-3 filed on April 18, 1996) in the names of Robert L. Heimann et al., and entitled "Corrosion Resistant Buffer System for Metal Products", which is a continuation in part of Non-Provisional U.S. Patent Application Serial No. 08/476,271 (Attorney Docket No. EL001RH-2 filed on June 7, 1995) in the names of Heimann et al., and corresponding  
15 to WIPO Patent Application Publication No. WO 96/12770, which in turn is a continuation in part of Non-Provisional U.S. Patent Application Serial No. 08/327,438, now allowed (Attorney Docket No. EL001RH-1 filed on October 21, 1994).

The subject matter of the instant invention is also related to copending and commonly assigned Non-Provisional U.S. Patent Application Serial No. \_\_\_\_\_ (Attorney Docket No. EL004RH-1), filed on even date herewith and entitled  
20 "Corrosion Protective Coatings".

The disclosure of the previously identified patent applications and publications is hereby incorporated by reference.

## 25 DETAILED DESCRIPTION

A lubricating grease is defined by National Lubricating Grease Institute (NLGI) as "a solid to semifluid product of dispersion of a thickening agent in a liquid lubricant. Additives imparting special properties may be included", e.g., refer to the Lubricating Grease Guide, 4th ed.; NLGI; Kansas City, MO; p.1.01; the disclosure of which is  
30 hereby incorporated by reference. For purposes of this invention, the terms grease and gel are used interchangeably wherein the term varies as a function of its application, e.g., dynamic greases or static gels. Typically, greases and gels fall broadly within the following formula:

35	Base oil	45-90%
	Thickener	5-25%
	Additives	1-30%

In an aspect of the invention, the inventive composition can comprise a gel  
40 which forms a self-supporting outer layer or skin. This type of gel has the capability of forming an outer layer or skin for the purpose of providing improved characteristics

such as a tack-free gel surface and resistance against washing away by rain or immersion. The outer skin can be achieved by any suitable means such as adding cross-linking polymers to the inventive composition. Examples of desirable methods for achieving cross-linking in the inventive composition include: 1) employing drying oils that exhibit an oxidative type curing mechanism, 2) by utilizing a moisture curing mechanism, 3) a reactive cure, 4) ultra-violet (UV) cure, 5) heat curing mechanism, among other chemistries. Depending upon the chemistry and environment, the selected method can be employed to obtain results that range from forming a self-supporting layer to hardening the entire inventive composition. Normally, the self-supporting layer is about 0.001 to about .05 inch thick depending on application. A cross-linking polymer system can be added to any base oil so long as the polymer to be crosslinked is partially miscible in the base oil, the crosslinked layer or hardened composition is resistant to the base oil and the system is compatible with the remaining components of the inventive composition. Examples of suitable base oils include at least one member from the group of naphthenic and paraffinic mineral oils, and synthetic oils such as polyalphaolefins, silicones, phosphate esters, fluorinated oils, polybutenes, polyalkylene glycols, alkylated aromatics, among others. Conventional drying oils can also be used to form a self-supporting layer or skin, e.g., linseed oil, and the oxidative curing can be accelerated by metallic catalysis such as cobalt naphthenate. Polymers such as oil modified epoxies or polyurethanes may also be utilized, e.g., Ketimine type moisture curing epoxy resin. While the amount of cross-linking polymer can be tailored to obtain the desired affect, typically the polymer corresponds to about .010 to less than about 50 wt.% of the inventive composition, depending on compatibility between the polymer and the gel base oil. At loadings greater than 50% the composition becomes increasingly like the polymer itself and gel-like characteristics decrease.

In a further aspect of the invention, the physical characteristics of the gel as applied are retained for an extended period, e.g., the gel is substantially non-crosslinked or lacking a self-supporting layer. In this aspect of the invention, the base oil of the grease/gel can comprise a polymer such as a polyurethane or epoxy and an oil such as linseed or a drying oil. Without wishing to be bound by any theory or explanation, it is believed that employing a relatively large amount of oil inhibits crosslinking in the polymer thereby causing the gel to retain its as applied characteristics.

The pH of the grease can be tailored to be compatible with the metal surface which is contacted with the grease or gel. That is, certain metals and alloys can become susceptible to caustic cracking when exposed to a relatively high pH, e.g, about 10 to about 14. In such cases, it may be appropriate to employ an alkali silicate such as sodium silicate with another silicate such as calcium silicate. Without wishing to be bound by any theory or explanation, the mechanism of protection follows the laws of chemical absorption and chemical affinity when the grease or gel contacts the surface being protected. The inventive grease will typically have a pH that ranges from about 7 to about 14. It is also believed that the presence of a relatively high pH in the grease



can hydrolyze, for example, zinc borate and silica, and equipotentialize the surface being protected. Depending upon the composition of the grease or gel and surface being protected, one or more components of the grease or gel can react with each other and/or the underlying surface to form a protective layer or film, e.g., when the inventive grease or gel is applied to a zinc containing surface a unique surface comprising an alkali zinc silicate crystallites within an amorphous phase composition can form.

Normally, a silicate will be employed as a thickener as well as a corrosion inhibitor. The silicates used for preparing the inventive grease/gel that is employed in lubricating applications such as working wire ropes are normally finely ground by milling the raw material or the final composition, e.g., milled to a particle size of about 1 to about 20 microns. Suitable silicates for working wire ropes among other applications can be selected from the group consisting of sodium silicate, calcium silicate, potassium silicate, lithium silicate, ammonium silicate, (each with various amounts of moisture of hydration and various ratios of silica to cations such as Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, among others), mixtures thereof, among others, and can be mixed together by any suitable means. The aforementioned silicates can be combined with or, in some cases, replaced by molybdates, phosphates, zirconates, titanates, vanadates, permanganates, pertechnetate, chromate, tungstate, nitrate, carbonates, aluminates, ferrates, mixtures thereof among others. To this silicate mixture, can be added at least one of a surfactant, coupling agent and at least one dispersion oil that are compatible with the base oil of the grease, e.g., silicone oil, PAO or polybutene, thereby forming an intermediate product. Typically, the coupling agent will comprise about 0.1 to about 2 wt.% of the grease and can be at least one member selected from the group consisting of organotitanates, organozirconates, organoaluminates and organophosphates. Surfactants include ethoxylates, pine oil, pine oil derivatives, tall oil, tall oil derivatives, acetylenic diols, long chain fatty acids, sulfosuccinates, alkyl sulfates, phosphates, sulfonates, long chain amines, quaternary ammonium compounds, organosilicons, fluorinated surfactants, mixtures thereof, among others. A suitable dispersion oil can be at least one member from the group consisting of linseed, boiled linseed, castor, canola, mineral, olive, peanut, sunflower, corn, soybean, cedar, pine, coconut, tung, vegetable, rapeseed, olive, jojoba, lanolin, meadow foam, cottonseed, sesame, palm, mixtures thereof, among others, and normally comprise about 1 to about 30 wt. % of the grease.

The previously described intermediate product can be dispersed or mixed with the remaining components of the grease, e.g, base oil, extreme pressure additive, among others. By adding the intermediate product to the remaining components, a corrosion resistant grease is obtained.

The aforementioned inventive intermediate product can be introduced into any suitable type of grease or gel such as:

- 1) Soap-Thickened Greases/Gels  
Aluminum Soap Grease

Hydrated Calcium Soap Grease  
Anhydrous Calcium Soap Grease  
Sodium Soap Grease  
Lithium Soap Grease

5        2) Soap-Complexed Greases/Gels

Aluminum Complexed Grease  
Calcium Complexed Grease [the amount of alkaline silicates that can be  
added to calcium complexed grease is relatively low in comparison to  
other greases]  
10        Barium Complexed Grease  
Lithium Complexed Grease

3) Non-Soap Greases/Gels

Mineral Oil Based Grease  
Vegetable Oil Based Grease  
15        Organo-Clay Grease  
Polyurea Grease  
Polyurea Complexed Grease

The thickener utilized in the soap-based greases is typically a saponification  
reaction product that is generated during the grease-making process. The saponification  
20        reaction can occur among at least one of the following components long-chained fatty  
acids, e.g. stearic acid, oleic acid, among others; fat, e.g., beef tallow; and an alkali  
component, e.g., aluminum, calcium, sodium, lithium hydroxide, among others. The  
aforementioned alkali component is normally used in a slight excess to facilitate driving  
the saponification reaction and to neutralize any remaining free acid. As the saponified  
25        product is cooled, the product can form a fibrous network through the base oil, e.g., a  
mineral or hydrogenated castor oil, thereby thickening the grease. For best results, the  
fatty acid or fat component is compatible with the base oil, the appropriate amount of  
thickener is employed, and the saponification reaction occurs at relatively dispersed  
locations within the base oil. For example, the aforementioned fibrous network may  
30        not be adequate if the saponification is conducted separately and then mixed into the  
base oil. Finally, the rate of cooling and amount of water present can impact the fibrous  
network formation rate.

A soap complexed grease is similar to the soap-thickened grease in that both  
types of greases rely upon the saponification reaction. However, the soap complexed  
35        greases have an additional reactant which becomes a component of the saponified  
product and facilitates forming the fibrous networks. The complexing or chelating  
reactant is normally a metal salt of a short chained organic acid, e.g., a calcium acetate,  
or a metal salt of an inorganic acid, e.g., lithium chloride. (The grease may also contain  
aluminum atom(s) which were part of the organic soap molecules, e.g. aluminum  
40        distearate and aluminum hydroxide) Total thickener contents, respectively, of the  
calcium, aluminum, and lithium complex greases are about 25 to about 35 wt.%, about

5 to about 9 wt.%, and about 12 to about 18 wt.%. In one aspect of the invention, the thickening soap may comprise sulphurized-phosphorized lard oil in lithium grease. This thickening soap can also function as an extreme pressure additive within the grease.

5 Non-soap based greases do not require the previously described saponification reaction to thicken the grease. Non-soap greases employ physical additives for thickening. While any suitable thickener can be employed, an example of a suitable thickener is organo-clay particles, or platelets of small organic or inorganic particles dispersed within the base oil. Further examples of thickeners comprise at least one of  
10 bentonite clay, fumed silica (aerogel), carbon black, powdered plastics, mixtures thereof, among others. In addition, surface modified thickeners may also be utilized. Normally, the thickener has a large surface area and typically a certain amount of an oil absorption capability.

Polyurea and polyurea complexed greases are related to the soap based greases  
15 in that reactions polymerize component materials, e.g., isocyanates and amines, to form the thickener, e.g., polyurea. However, the polyurea normally does not form fibrous networks to the extent of soap based greases. The complexed polyureas utilized the same types of complexing agents as the complexed soap based greases.

The following types of additives may be incorporated into greases or gels to  
20 achieve a variety of desired properties: rust inhibitors, antioxidants, soaps, odor modifiers, tackiness agents, structure modifiers, metal deactivators or corrosion inhibition for non-ferrous metals, solid lubricants (such as graphite, zinc oxide, borax, among other conventional solid lubricants), phosphate esters, polytetrafluoroethylene, dithiophosphates, dithiocarbonates, antimicrobial agents, mixtures thereof, among other  
25 suitable additives. Examples of suitable rust inhibitors comprise at least one member selected from the group consisting of fatty acids, sulfonates, amines or amine phosphates, amides of fatty acids, succinates, benzotriazoles, tolutriazoles, mercaptobenzothiazole, thiadiazoles, metal carboxylates, mixtures thereof, among others. Examples of suitable antioxidants comprise at least one member selected from  
30 the group consisting of aromatic amines, hindered phenols, diphenylamine, phenyl alpha-naphthylamine, 2,6-di-t-butylphenol, phenothiazine, alkylated diphenylamines, alkylated phenyl alpha-naphthylamines, 2,6-di-t-butyl-p-cresol (BHT), polymeric BHT, peroxide decomposers, mixtures thereof, among others to inhibit natural or high temperature oxidation of the composition. The formulation can also include additives to  
35 improve ultraviolet (UV) light stability such as Tinuvin (Ciba Geigy), a substituted hydroxyphenyl benzotriazole. Examples of soaps include lithium stearate, aluminum stearate, calcium stearate, or zinc stearate. Soaps may be utilized to impart added lubricity, heat resistance, or moisture resistance. Examples of suitable tackiness agents comprise at least one member selected from the group consisting of high molecular  
40 weight hydrocarbons, rubber latex, polybutenes, estergums and terpene resins mixtures thereof, among others. Examples of suitable structure modifiers comprise at least one

member selected from the group consisting of glycerol, alcohols, glycols, fatty acids, water, alkali sulfonaphthenates, mixtures thereof, among others. Examples of suitable anti-microbial agents comprise at least one member selected from the group consisting of zinc borate, silver, quaternary ammonium compounds, mixtures thereof, among  
5 others. Other environmentally less desirable anti-microbial compounds include compounds of mercury, tin, antimony, and mixtures thereof. The additives can also comprise at least one member selected from the group consisting of surfactants, wetting agents, surface active agents, pine oil, derivatives, tall oil and derivatives, ethoxylates, acetylenic diols, silicones, silanes, fatty oils or acids with a phosphate adduct,  
10 sulfurized fatty oils, molybdenum disulfide, tungsten disulfide, mixtures thereof, among others. The total amount of these additives normally does not accumulate to more than about 5 wt.% of the total grease formulation. The inventive composition can also include a substance for imparting conductivity to the composition such as graphitic carbon, conductive polymers, metal powder or flake mixtures thereof, among others.  
15 The amount of conductive component normally ranges from about 15 to about 45 wt.% of the inventive composition.

While the inventive grease/gel can provide a physical barrier from a corrosive environment, the grease can also supply a silica/silicate product that imparts the previously described corrosion-inhibiting properties. Depending upon the composition  
20 of the metal surface, composition of grease/gel applied to the surface, temperature and length of time the composition is in contact with the metal surface, surface pH, at least a portion of the grease can interact with the metal surface. The interaction can produce a mineral-like surface coating, e.g, less than about 100 Angstroms thick, characterized by unique crystallites, e.g, an alkali zinc silicate, within an amorphous matrix. A more  
25 detailed description of mineral layers and precursors thereof can be found in the aforementioned copending and commonly assigned U.S. Patent Applications; the disclosure of which was incorporated by reference.

While the inventive grease can be employed in connection with a virtually unlimited array of surfaces, desirable results have been obtained when the grease is  
30 employed upon a zinc containing surface or alloy. The inventive grease can be employed in a virtually unlimited array of applications such as upon pipe in order to inhibit corrosion under insulation, wire rope and strand products during manufacture or afterwards by injecting the grease, and applied to the exterior armor/sheathing of electrical and optical fiber cables that are exposed to marine environments as well as  
35 mechanical force cables such as those employed in automobiles, boats and aircraft. The invention is also useful in cable applications where RFI-EMI properties are important such as some undersea cables. The inventive grease can also be employed as cutting/buffing/grinding fluids for ceramics/metals, protect and lubricate lead alloy battery terminals, protect and lubricate lock assemblies, and protect coiled metal rolls or  
40 stack metal sheet from corrosion, among many other applications where corrosion resistance and/or lubrication are useful. The inventive greases or gels can be applied to

the above users via spray, trowel, glove, brush, immersion, pressure injection, or pumping.

The following Examples are provided to illustrate not limit the scope of the invention as defined in the appended claims.

5

#### EXAMPLE 1

The formulation listed below in Table 1 was produced by adding powdered materials to the PAO base oil, i.e., polymerized 1-decene. The PAO oil was poured into a 1 quart stainless steel bowl. The powdered materials were then added to the PAO and mixed by hand.

10

TABLE 1		
COMPONENT	SUPPLIER	AMOUNT % BY WT.
PAO base oil	Nye Lubricants	53.5%
15 Silica	Nye Lubricants	9.8
G sodium silicate	PQ Corp.	30.0
Zinc Borate	U.S. Borax	5.0
p-Hydroxy Aniline	Mallinckrodt Chemical	0.7
Indigo Blue Dye	Tricon Colors Inc.	1.0

20

This composition, when applied to a standard ACT electrogalvanized steel test panel (E60 EZG 60G 2 side 03x06x030) to a thickness of 1/16 inch, protects from red corrosion for a minimum of 1000 hours in accordance with ASTM B117 salt spray exposure. When the composition was removed from the panel after a minimum of 24 hours by carefully scraping off the excess and then washing with naphtha, an average of 192 hours of ASTM B117 salt spray exposure was obtained prior to the appearance of red corrosion products compared to 120 hours for untreated control samples.

25

Depending upon the surrounding environment, improved corrosion resistance can be obtained by omitting p-Hydroxy Aniline. Further, the corrosion resistance of a PAO based grease or gel can be improved by the adding at least one of sodium molybdate, sodium carbonate, and sodium silicate.

30

#### EXAMPLE 2

A second formulation substantially the same as that described in Example 1 was prepared with the exception that p-Hydroxy Aniline was omitted. The removal of the p-Hydroxy aniline improved the environmental acceptability of the formulation without adversely impacting the corrosion resistant properties of the grease.

35

A third formulation was prepared by omitting the zinc borate. While silica was employed as a thickener, e.g., refer to the Standard Base Formulation in Table 2 below, the presence of silica and a silicate can have a desirable combined effect upon the

40

corrosion resistant properties of the grease. Zinc borate functions as a fire retardant and a microbiological inhibitor and, therefore, can be removed with its attendant properties.

### EXAMPLE 3

The following formulas were produced to compare the corrosion resistance of the inventive greases to a base formulation.

TABLE 2  
--BASE FORMULATION--

COMPONENT	SUPPLIER	AMOUNT (WT%)
PAO	Durasyn 174 (Amoco Oil Co.)	88.4%
silica	Cabosil TS720 (Cabot Corp.)	11.1%
dye	T-17N Dye (DayGlo Color Corp)	0.5%

--CORROSION RESISTANT FORMULATION 1--

PAO	Durasyn 174 (Amoco Oil Co.)	57.3%
PAO	Durasyn 166 (Amoco Oil Co.)	14.3%
silica	Cabosil TS720 (Cabot Corp.)	7.3%
zinc borate	Borogard ZB (U.S. Borax)	4.1%
sodium silicate	G Grade (PQ Corp.)	16.3%
indigo blue dye	Tricon Color Corp.	0.7%

--LUBRICATIVE FORMULATION 1--

PAO	Durasyn 174 (Amoco Oil Co.)	58.4%
polytetrafluoroethylene	Fluro 300 (Micro Powders Inc.)	40.9%
indigo blue dye	Tricon Color Corp.	0.1%
organo zirconate	Ken-React NZ-12 Kenrich Petrochemical, Inc.	0.6%

--CORROSION RESISTANT FORMULATION 2--

silicone oil	Dow Corning 200	75%
silica	Cabosil TS729 (Cabot Corp.)	15%
sodium silicate	G grade (PQ Corporation)	10%

Corrosion Formulation 1 was prepared by mixing the zinc borate and sodium silicate together in the manner described in Example 1. The borate/silicate blend was added to Durasyn 166 PAO. The silica was mixed with Durasyn 174 PAO. The two PAO mixtures were then combined. The dye was then added to the combined PAO mixtures.

Lubricative Formulation 1 was prepared by first treating the Fluoro 300 with a 2.3 weight % solution of NZ-12 in 2-propanol, and allowing the 2-propanol to evaporate. The treated Fluoro 300 was then mixed into the Durasyn 174 by hand. After thorough mixing, the Indigo blue dye was introduced. While both Formulations have a wide range of uses, Lubricative Formulation 1 is particularly useful as an emergency brake cable lubricant.

Corrosion Formulation 2 was formed substantially in the same manner as Corrosion Resistant Formulation 1. If desired, the sodium silicate of the previously identified Formulations can be mixed with or substituted for calcium silicate, trisodium phosphate, sodium bicarbonate, among others, in order to obtain a grease/gel with a lower pH. Further, if desired the sodium silicate can be at least partially replaced by polytetrafluoroethylene to improve its lubricative properties.

#### EXAMPLE 4

Corrosion Resistant Formulation No. 1 was coated upon a standard ACT electrogalvanized steel test panel (E60 EZG 60G 2 side 03x06x030) by applying an excess and smoothing with a gate type applicator to leave a 1/16 inch thick layer. The grease/gel remained in contact with the test panel for a period of about 24 hours. The grease/gel was removed from one-half of the test panel by light scrapping and washing with naphtha.

The test panels were then tested under a salt spray environment in accordance with ASTM Procedure B117. The area where the coating had been removed lasted about 216 hours before 5% of the surface area was covered with red rust. The grease/gel coated area of the test panel had no visible red rust after 1,000 hours of salt spray exposure.

#### EXAMPLE 5

The following formula was prepared and applied to an outdoor above ground piping which was subsequently covered with an external layer of insulation.

COMPONENT	SUPPLIER	AMOUNT
Polyalphaolefin Base Oil	Durasyn 174/Amoco Oil Co.	81.7 wt. %
Silica	Cabosil TS-720/Cabot Corp.	4.7%
Synthetic Calcium Silicate	Hubersorb 600/J.M. Huber Corp.	11.7%
Polybutene Based Tackifier	IdaTac M256/Ideas, Inc.	1.5%
Dye	Indigo/Tricon Color Corp.	0.4%

The Hubersorb 600 and Cabosil TS-720 were dry mixed together in a covered 5 gallon pail for 5 minutes and then the mixed composition was added to the Durasyn 174 base oil in successive additions until all the powder had been added. The resulting mixture was then mixed for an additional 20 minutes.

After combining the Durasyn, IdaTac M256 was added volumetrically from a syringe and mixing was continued for 15 minutes. Finally, the Indigo dye was added and the composition was mixed for an 15 additional minutes.

5 The final composition had a penetration number of 317 as determined in accordance with ASTM-D217. The resulting composition was applied to a standard cold roll steel panel in a clean/unpolished condition to obtain a film thickness of 1/16 inch. After 24 hours of exposure to salt spray in accordance with ASTM B-117 no corrosion had occurred beneath the film.

10 The composition was also applied to a rusted 2.5 inch diameter steel pipe that had been wire brushed to remove loose scale. The film was applied to approximately 1/16 inch thickness and the pipe was not covered with insulation. After 4 weeks of outdoor exposure (including rain and wind events) no noticeable degradation, or loss of coated material from the pipe was observed.

#### 15 EXAMPLE 6

The above formulation for CUI application is adapted for use on an automotive/industrial battery terminal to control the corrosion of battery posts. A battery terminal corrosion protectant is prepared by removing the indigo dye and adding up to about 30 % by weight conductive carbon black to the aforementioned composition. (the conductive material will provide a dark color).

#### EXAMPLE 7

Amounts of Cabosil TS-720, Hubersorb 600, Lithium Hydroxystearate, S-395-N5 and Ackrochem 626 were measured out in quantities sufficient to prepare a 350 g. total batch. These powders were then dry mixed and then added to the Lubsnap 2400 oil which had been preheated to 110° C. The composition was then mixed with a Premier Mill Series 2000 Model 84 Laboratory Dispersator at N3000 rpm utilizing a 2-inch ZNOCO Desron dispersion blade for 15 minutes. At this time the Lubrizol 3108 and Tallicin 3400 was added and mixed for another 15 minutes. A composition containing the following components was prepared in accordance with Example 1, and used to protect wire rope and stranded cables:

COMPONENT	SUPPLIER	AMOUNT
Napthenic Mineral Base Oil	Lubsnap 2400/Tulco Oils Inc.	67.5%
35 Silica	Cabosil TS-720/Cabot Corp.	6.3%
Synthetic Calcium Silicate	Hubersorb 600/J.M. Huber Corp.	16.2%
Lithium Hydroxystearate	Witco Corp.	2.5%
Polyisobutylene	Indopol H-100/Amoco	2.5%
Wetting Agent**	Additive 3108/Lubrizol Corp.	2.5%
40	Tallicin 3400/Pflaumer Brothers, Inc.	



Micronized Polyethylene	S-395-N5/Shamrock Inc.	2%
Blue Dye	Ackrochem 626/Ackron Chemical Co.	0.5%

5      \*\*Tallicin 3400 is sold commercially as being a proprietary composition. Examples of other suitable wetting agents comprise at least one member selected from the group consisting of pine oils, tall oil, pine oil derivatives, tall oil derivatives, mixtures thereof, among others.

#### EXAMPLE 8

10      The following formula was prepared in accordance with Example 1, and applied to a steel panel to form an outer self-supporting layer that was subsequently covered with an external layer of wollastonite insulation:

	COMPONENT	SUPPLIER	AMOUNT
15	Polyalphaolefin Base Oil	Durasyn 174/Amoco Oil Co.	51.6%
	Linseed Oil	commercial	30.0%
	Cobalt Naphthenate	commercial	0.1%
	Silica	Cabosil TS-720/Cabot Corp.	4.7%
	Synthetic Calcium Silicate	Hubersorb 600/J.M. Huber Corp.	11.7%
20	Polybutene Based Tackifier	IdaTac M256/Ideas, Inc.	1.5%
	Dye	Indigo/Tricon Color Corp.	0.4%

#### EXAMPLE 9

25      The benefit of adding polymer to an inventive composition was demonstrated by adding a polymer gel to a base gel formula that was prepared in accordance with Example 1 and has the following formula: -

	COMPONENT	BASE GEL SUPPLIER	AMOUNT
30	Polyalphaolefin Oil	Durasyn 174 (Amoco)	55.2 wt. %
	Fumed Silica	Cabosil TS-720 (Cabot Corp.)	9.8 wt. %
	Sodium Silicate	G Grade (PQ Corp.)	30 wt. %
	Zinc Borate	Borogaro ZB (U.S. Borax)	5 wt. %

#### POLYMER GEL

35      Polyurethane polymer was added to the gel by mixing ACE .16381 Polyurethane Clear Finish (supplied by Westlakes) with the aforementioned base gel in a 1:15 ratio by weight respectively. The gel and polymer compositions were mixed with a spatula for approximately 15 minutes to form a homogeneous mixture. Standard 0.032 in. X 3  
40 in. X 6in. cold roll steel panels (supplied by ACT) were coated with a 0.05 inch thick

layer over a 4 inch by 3 inch area. One panel was coated with the Base Gel Formula and one panel was coated with the Polymer Gel containing Formula.

In order to illustrate the effectiveness of the polymer gel formula to protect metal surfaces from corrosion under insulation, a piece of wollastonite mineral pipe insulation (approximately 0.25 inches X 1.5 inches X 5 inches) was placed on each gel coated panel with the broad surface contacting the gel. A 71 gram weight was placed on top of each piece of insulation and the panels were allowed to sit at ambient conditions for 48 hours. At 48 hours, the weight and insulation was removed and the following observations and measurements were made.

GEL TYPE	INITIAL WEIGHT (g) OF INSULATION	FINAL WEIGHT (g) OF INSULATION	OIL ABSORPTION (g) INTO INSULATION
Base Gel	8.085	9.4412	1.356 g.
Polymer Gel	7.562	7.673	0.111 g.

The layer of Base Gel beneath the insulation was visibly observed to have cracks or separations in the gel due to oil loss from the gel, e.g., the oil was absorbed by the adjoining insulation. In contrast, no cracks were noted in the polymer containing gel composition. As illustrated above, the polymer gel reduced oil loss or migration into the insulation to less than one tenth of the loss that the Base Gel exhibited.

This Example was repeated by replacing the polyurethane polymer with epoxy resins supplied by Reichhold Chemical as EPOTUF 690 and 692. The amount of epoxy was 20 wt.% of the total composition.

#### EXAMPLE 10

A substantially biodegradable formulation having the following formulation was prepared:

COMPONENT	SUPPLIER	AMOUNT
Polyol Ester	Emkarate 1950/ICI Chemicals	67.5 wt. %
Fumed Silca	TS-720 /Cabot Corp.	5.4 wt. %
Calcium silicate	Hubersorb H-600/J.M. Huber Corp.	3.6 wt. %
Lithium Stearate	Witco Corporation	14.3 wt. %
polyethylene	S-395-N5 /Shamrock Technologies	3.6 wt. %
polybutene	Indopol H-300/Amoco Chemical	3.6 wt. %
hydrated lime	Mississippi Lime Co.	2.0 wt. %

A 350 gram batch of the above composition was prepared by heating the Emkarate 1950 base oil to a temperature of 110°C, and then mixing in the pre-mixed powdered components of the grease in a Premier Mill Series 2000 Model 84 Laboratory

Dispersator at N3000 rpm utilizing a 2 inch INDCO Design D dispersion blade for 15 minutes. Finally, the Indopol H-300 polybutene was added and the composition was mixed for another 15 minutes. After allowing the composition to cool to room temperature, the penetration in accordance with ASTM-D217 was measured and determined to be 277.

Three standard 0.032 in. X 3 in. X 6 in. cold roll steel panels (ACT Laboratories) were rinsed with Naphtha and wiped with a Kimwipe prior to applying 2.25 grams to the entire front panel surface (N 0.008 in. thick) with a Micrometer gate applicator. The coated panels were exposed to salt spray conditions (20% aqueous sodium chloride solution) as established in MIL-G-18458B for 10 days. After 10 days, the grease was wiped off and the panels were inspected for red corrosion farther than 0.25 inches from the edges of the panel. Each panel had less than 7 corrosion spots which exceeded 1 mm in diameter, and surface coverage by corrosion did not exceed 5%.

#### EXAMPLE 11

The following Example demonstrates that certain naturally occurring base oils are combinable with synthetic base oils. This Example also illustrates formation of a coating/film having a relatively firm or self-supporting outer surface and uncured material underlying the outer surface. The following compositions were prepared by in accordance with Example 7.

#### -COMPOSITION A-

AMOUNT	COMPONENT	SUPPLIER
55-60/28-30 wt.% 2:1 ratio	Linseed oil/PAO	ADM/Amoco
0.75-1.0 wt.%	calcium silicate-Hubersorb 600	J.M. Huber Corp
2.0 wt.%	amber wax-Bareco Ultraflex	Bareco-Petrolite
6 - 8 wt.%	fumed silica-Cabosil 610	Cabot Corp.

#### -COMPOSITION B-

AMOUNT	COMPONENT	SUPPLIER
55-60/28-30wt.% 2:1 ratio	Linseed oil/PAO	ADM/Amoco
0.75-1.0 wt.%	calcium silicate-Hubersorb 600	J.M. Huber Corp
5.0 wt.%	amber wax-Bareco Ultraflex	Bareco-Petrolite
6 - 8 wt.%	fumed silica-Cabosil 610	Cabot Corp.

These compositions were applied by using a drawdown gate onto an ACT steel test panel. The composition formed a coating/film in about 24 hours by drying under ambient conditions. The characteristics of the coating/film were an outer self-supporting and resilient layer. The portion of the coating/film between the outer layer and test panel remained uncured in a substantially unchanged physical state. When applied to the test panel the coating/film imparted enhanced corrosion resistance to

panel, in that the outer layer is water resistant and repellent while the underlying uncured portion inhibits the ability for corrosive materials to attack the panel.

The corrosion resistance of the coating/film was demonstrated in accordance with ASTM Test No. B-117 (salt spray) and D2247 (humidity). Test panels coated, respectively, with compositions A and B were tested together at 500 hrs., 750 hrs., and 1000 as per ASTM B-117. The outer self-supporting layer remained intact, was not penetrated by corrosion material, and remained flexible. The portion of the coating/film under the outer layer remained gel-like after 1,000 hrs of salt exposure. No rust was observed via visual detection after 1,000 hours of ASTM B-117 testing.

Test panels coated, respectively, with Compositions A and B were tested at 1000 hrs as per ASTM D2247. Results similar to the previous ASTM B-117 were obtained; except that the outer layer was more flexible. No rust was observed via visual detection after 1,000 hours of ASTM D2247 testing.

In addition to corrosion resistance, panels coated with Composition B were evaluated for temperature and pressure resistance. In test two panels were coated with Composition B, allowed to cure for 48 hrs. under ambient conditions and placed into an All American brand Model No. 25X pressure sterilizer, manufactured by Wisconsin Aluminum Foundry Co., at 240 F and 2X atmospheric pressure for a period of 24 hrs. The only visually detectable affect was an increased darkening of the outer self-supporting layer. The temperature and pressure resistance of a panel coated with Composition B that had undergone 750 hrs. in the ASTM B117 Salt Spray was also evaluated. Similar to the aforementioned results, the only reportable change was a darkening of the outer self-supporting layer.

#### EXAMPLE 12

This Example illustrates a composition, which includes syntethic and naturally occuring oils, that forms a self-supporting layer. The following composition was prepared by Example 7:

COMPONENT	SUPPLIER	AMOUNT
Linseed oil	ADM	50-60 wt.%
polybutene	Indopol H-50/Ideas Inc.	20-30 wt.%
calcium silicate	Hubersorb 600/Huber Corp.	2-8wt.%
wax	Ultraflex Amber Wax	0-4wt.%
	(Bareco Petrolite)	
fumed silica	TS610 or TS720	5-8wt.%
	(Cabot Corp.)	
polyethelene	S-395-N5	0-4wt.%
	(Shamrock Tech.)	

The viscosity and tackiness properties of the above composition can be improved by adding about 1-4wt.% lithium stearate, e.g., such as that supplied by Reagens of Canada. The lithium stearate can be added to the composition by being introduced and admixed along with the other components of the composition.

### EXAMPLE 13

This Example illustrates a non-migrating composition that can be employed to reduce, if not eliminate, corrosion under insulation and can be applied to a wet surface. The following composition was prepared by Example 7:

COMPONENT	SUPPLIER	AMOUNT
Polybutene	Indopol H-50 - Ideas Inc.	54-64 wt. %
Epoxy Resin	EP08YF 692 - Reichhold Chemical	15-25wt. %
Fumed Silica (Cab-o-sil)	TS720 - Cabot Corp.	3-8wt. %
Calcium Silicate	Hubersorb 600 - Huber Corp.	4-10wt. %
Lithium Stearate	Reagens - Reagen Co. Canada	4-10wt. %

The above composition was applied to a wet metallic substrate (test panel) without adversely impacting the adhesion to the substrate. The composition was also applied to a metallic substrate while the substrate was immersed in water. The characteristics of the composition can be tailored by incorporating heat-bodied linseed oil, e.g., about 5 to about 10wt.% of OKO-S70 supplied by ADM Corp. If desired, about 5 to about 10 wt. % silicone resin could also be incorporated into the composition, e.g., the silicone supplied by GE (General Electric) of Waterford NY.

### EXAMPLE 14

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of galvanize metal substrates. The interaction was detected by using ESCA analysis in accordance with conventional methods.

Analytical conditions for ESCA:

Instrument	Physical Electronics Model 5701 LSci
X-ray source	Monochromatic aluminum
Source power	350 watts
Analysis region	2 mm X 0.8 mm
Exit angle*	50°
Electron acceptance angle	±7°
Charge neutralization	electron flood gun
Charge correction	C-(C,H) in C 1s spectra at 284.6 eV

\* Exit angle is defined as the angle between the sample plane and the electron analyzer lens.

Coatings were made up based on the ingredients and formulation methods shown in Example 10. Different base oils and base oil combinations, alkali silicate types, silicate amounts, and substrates were used to represent a cross section of possible ranges. The different base oils comprised polyalphaolefin (polymerized 1-decene) and linseed oil. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 1% to 50% wt to show the range of possible concentrations. Each set of coatings were applied onto both cold rolled and galvanized steel panels.

Each formulation was mixed together and applied onto the given substrate at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24 hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.

#### Formulations used for ESCA/XPS analysis

Sample #	1	2	3	4	5	6	7	8
Durasyn 174	49.3	44.3	49.3	44.3	87	79.2	70.4	44
wt.%(PAO)								
Linseed Oil	49	44	49	44	0	0	0	0
wt.%(Fumed Silica)								
	0.7	0.7	0.7	0.7	12	10.8	9.6	6
wt.%(Sodium silicate)								
	1	10	0	0	0	0	20	50
wt.%(Calcium silicate)								
	0	0	1	10	1	10	0	0
wt.%(wt.%)								

ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the coating. Every sample

measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. Higher binding energies (>103.8 eV) indicate precipitated silica due to the charging effect of the silica which has no chemical affinity to the surface. The resulting spectra show overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

#### EXAMPLE 15

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of lead substrates. The interaction was detected by using ESCA analysis in accordance with conventional methods.

Coatings were made up based on the ingredients shown in table shown below. Different alkali silicate types and silicate amounts were used to represent a cross section of possible ranges. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 5% to 50% wt to show the range of possible concentrations. Each coatings was applied onto lead coupons. Prior to gel application, the lead coupons cut from lead sheets (McMasters-Carr) were cleaned of its oxide and other dirt by first rubbing with a steel wool pad. The residue was rinsed away with reagent alcohol and Kim wipes.

Each formulation was mixed together and applied onto a lead coupon at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24 hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.

Formulations used for ESCA/XPS analysis on lead panels

Sample #	1	2	3	4
Durasyne 174	89	74	89	44
wt. %				
Fumed Silica	6	6	6	6
wt. %				
Sodium	0	0	5	50

silicate				
wt. %				
Calcium	5	20	0	0
silicate				
wt. %				

ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show some overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica. The primary binding energy for all of these samples were in the range of 102.1 to 102.3 eV.

#### EXAMPLE 16

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of GALFAN® substrates (a commercially available alloy comprising zinc and aluminum). The interaction was detected by using ESCA analysis in accordance with conventional methods.

Coatings were made up based on the ingredients shown in table shown below. Different alkali silicate types and silicate amounts were used to represent a cross section of possible ranges. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 5% to 50% wt to show the range of possible concentrations. Each coatings was applied onto galfan coated steel coupons. Prior to gel application, the galfan coupon, cut from galfan sheets (GF90, Weirton Steel), were rinsed with reagent alcohol.

Each formulation was mixed together and applied onto a lead coupon at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24 hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.



## Formulations used for ESCA/XPS analysis on Galfan® panels

Sample #	1	2	3	4
Durasyn 174	89	74	89	44
wt. %				
Fumed Silica	6	6	6	6
wt. %				
Sodium silicate	0	0	5	50
wt. %				
Calcium silicate	5	20	0	0
wt. %				

ESCA was used to analyze the surface of each of the substrates. ESCA  
 5 detection of the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by  
 10 a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show some overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

#### 15 EXAMPLE 17

The following Example demonstrates formation of the previously described mineral layer as a result of a component of the grease/gel interacting with the surface of copper substrates. The interaction was detected by using ESCA analysis in accordance with conventional methods.

20 Coatings were made up based on the ingredients shown in table shown below. Different alkali silicate types and silicate amounts were used to represent a cross section of possible ranges. Two types of alkali silicates were also used, sodium and calcium silicate. The concentration of the alkali silicate was also varied from 5% to 50% wt to show the range of possible concentrations. Each coatings was applied onto  
 25 galfan coated steel coupons. Prior to gel application, the copper coupons cut from copper sheets (C110, Fullerton Metals) were rinsed with reagent alcohol.

Each formulation was mixed together and applied onto a lead coupon at a thickness between 5 and 10 mils. The coatings were allowed to set for at least 24 hours and then removed from the substrate. Removal was accomplished by first scraping off the excess coating. The residual coating was washed with the base oil used in the formulation to absorb any of the silica or silicates. Finally the excess oil is removed by washing with copious amounts of naphtha. Not adequately removing the silica from the residual coating, will leave behind a precipitate in the subsequent naphtha washing, making any surface analysis more difficult to impossible.

Formulations used for ESCA/XPS analysis on copper

Sample #	1	2	3	4
Durasyn 174	89	74	89	44
wt. %				
Fumed Silica	6	6	6	6
wt. %				
Sodium silicate	0	0	5	50
wt. %				
Calcium silicate	5	20	0	0
wt. %				

ESCA was used to analyze the surface of each of the substrates. ESCA detects the reaction products between the metal substrate and the coating. Every sample measured showed a mixture of silica and metal silicate. The metal silicate is a result of the reaction between the metal cations of the surface and the alkali silicates of the coating. The silica is a result of either excess silicates from the reaction or precipitated silica from the coating removal process. The metal silicate is indicated by a Si (2p) binding energy (BE) in the low 102 eV range, typically between 102.1 to 102.3. The silica can be seen by Si(2p) BE between 103.3 to 103.6 eV. The resulting spectra show some overlapping peaks, upon deconvolution reveal binding energies in the ranges representative of metal silicate and silica.

THE FOLLOWING IS CLAIMED:

1. A grease or gel composition comprising:  
base oil about 70 to about 90 wt%  
5 thickener about 5 to about 20%; and,  
additives about 1 to about 10%.
2. A grease or gel composition consisting essentially of:  
base oil about 70 to about 90 wt%  
10 thickener about 5 to about 20%; and,  
additives about 1 to about 10%.
3. The grease or gel composition of Claim 1 or 2 wherein the base oil  
comprises at least one of PAO, silicone, animal, vegetable, fish, petroleum derived and  
15 synthetic oils, phosphate esters, fluorinated oils and mixtures thereof.
4. The grease or gel composition of Claim 1 or 2 wherein the thickener  
comprises silica and at least one silicate. Grease or gel composition of Claim 1 or 2  
consisting of an environmentally preferred lubricant (EPL) that is biodegradable and/or  
20 non-toxic to include animal, vegetable, or fish oils, polybutenes, synthetic esters,  
polyalphaolefin oils, and polyalkylene glycols.
5. The grease or gel composition of Claim 1 or 2 wherein the additive  
comprises at least one surfactant or coupling agent selected from the group consisting  
25 of organotitanates, organozirconates, organo aluminates, organophosphates; long chain  
fatty acids, sulfosuccinates, alkyl sulfates, phosphates, sulfonates, long chain amines,  
quaternary ammonium compounds, organosilicons, pine oil, pine oil derivatives, tall  
oil, tall oil derivatives, ethoxylates, acetylenic diols, fluorosurfactants, and mixtures  
thereof.  
30
6. A grease or gel composition consisting essentially of about 45 to 60  
wt.% PAO, an additive comprising polytetrafluoroethylene, and at least one member  
selected from the group consisting of an organo zirconate, organo titanate, organo  
aluminate, and zinc borate.  
35
7. A grease or gel composition consisting essentially of about 45 to 60  
wt. % Polybutene, an additive comprising polytetrafluoroethylene, and at least one  
40 member selected from the group consisting of an organo zirconate, organo titanate,  
organo aluminate, and zinc borate.

8. Grease or gel composition of Claim 1 or 2 consisting of an environmentally preferred lubricant (EPL) that is biodegradable and/or non-toxic to include animal, vegetable, or fish oils, polybutenes, synthetic esters, polyalphaolefin oils, and polyalkylene glycols.

9. A grease or gel composition comprising a combination of at least one base oil selected from the group consisting of polyalphaolefin, polyglycol, silicone, and polyol ester, at least one alkali silicate, silica, an antimicrobial agent and an optional tackifier.

10. A method for reducing corrosion comprising:  
applying the composition of Claim 1, 2, 6, 7 or 9 upon a substrate comprising at least one member selected from the group consisting of wire rope, anchor connecting links, pipes, strand, jacketed cables or tendons, battery terminals and mechanical latch mechanisms, such as nautical water tight door latches.

11. The method of Claim 10 wherein at least a portion of the substrate is covered by insulation.

12. The method of Claim 10 wherein at least a portion of the applied composition chemically cross-links.

13. The composition of Claim 1, 2, 6, 7 or 9 containing at least one electrically conductive component from carbon black, metallic particles, conductive polymers.

14. The composition of Claim 1, 2, 6, 7 or 9 further comprising an extreme pressure additive and/or anti-wear additive, selected from the group consisting of polyethylene, polyvinylidene difluoride, polytetrafluoroethylene, polyvinyl fluoride, phosphate esters, dithiophosphates, dithiocarbonates, calcium carbonate, zinc stearate, ammonium molybdate, chlorinated paraffins, graphite, molybdenum disulfide, tungsten disulfide, zinc oxide, borax, boron nitride, tricresyl phosphate, triphenyl phosphorothionate, fatty acid esters; sulfurized or phosphite adducted fatty oils, fatty acids, or fatty acid esters.

15. The composition of Claim 1, 2, 6, 7 or 9 further comprising a tackifier selected from the group consisting of polybutene, polyterpene resins, rosin esters, modified terpene resins.

16. The composition of Claims 1, 2, 6, 7 or 9 further comprising at least one member selected from the group consisting of lithium stearate, wax, lime, polyurethane, linseed oil and a dye.

5 17. Composition of 1, 2, 6, 7, or 9 comprising at least one of lanolin oil or lanolin wax.

18. The composition of Claim 9 further comprising a polyurethane resin.

10 19. The composition of Claim 9 further comprising an epoxy resin.

20. The composition of Claims 1, 2, 6, 7, or 9 further comprising at least one anti-oxidant or light stabilizer selected from the group consisting of aromatic amines, hindered phenols, diphenylamine, phenyl alpha-naphthylamine, 2,6-di-t-butylphenol, phenothiazine, alkylated diphenylamines, alkylated phenyl alpha-naphthylamines, 2,6-di-t-butyl-p-cresol (BHT), polymeric BHT, peroxide decomposers, or a substituted hydroxyphenyl benzotriazole.

20 21. A method for improving the corrosion resistance of metal surface comprising applying the composition of Claims 1, 2, 6, 7, or 9, wherein said applying comprises at least one of spraying, pumping, hand applying, brushing, trowelling, gloved, immersing, or pressure injected.

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/01857

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10M169/00 C10M169/06 //C10N30:12,C10N50:10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 11245 A (EXXON RESEARCH AND ENGINEERING COMPANY) 18 April 1996	1-3, 10, 14, 15, 21
Y	see page 1, paragraph 2 see page 2, last paragraph see page 5, paragraph 2 - paragraph 3 see page 6; example C see page 7	4
Y	US 3 525 689 A (R. MAROTTA) 25 August 1970 see column 7, line 28 - line 42; claim 1	4
X	US 3 833 513 A (J.F. PRINCETON) 3 September 1974 see claims 1, 2	1-3, 5, 10, 20
X	US 4 735 146 A (W.G. WALLACE) 5 April 1988 see column 9; claims 1, 2; example 1	1-3, 8, 14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

28 May 1998

Date of mailing of the international search report

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Hilgenga, K

# INTERNATIONAL SEARCH REPORT

Int. Jonal Application No

PCT/US 98/01857

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 12770 A (ELISHA TECHNOLOGIES CO.) 2 May 1996 cited in the application see page 28, paragraph 2 - page 29, paragraph 3 ----	1-4, 6-10,21
X	DE 40 41 156 A (KAJO SCHMIERSTOFF) 25 June 1992 see claims 1-4 ----	1-3,8,20
X	WO 92 00368 A (CASHEM) 9 January 1992 see page 16; examples 1,2,8,9 see claims 1,2,5,7 ----	1-4,8,20
X	DE 44 23 203 A (ALPS ELECTRIC) 12 January 1995 see page 3, line 18 - line 21 ----	1-3,5,16
X	DATABASE WPI Section Ch, Week 9440 Derwent Publications Ltd., London, GB; Class A17, AN 94-322436 XP002015933 & JP 06 248 287 A (NTN CORP) see abstract ----	1-3,8,13
X	US 4 406 800 A (J.B. CHRISTIAN) 27 September 1983 see column 5; examples 7,8 ----	1-3,8,14
X	US 4 859 352 A (J.A. WAYNICK) 22 August 1989 see claim 12 ----	1-3,5,8, 14,20
X	WO 95 19410 A (CASHEM) 20 July 1995 see page 14; examples 1-3 see claims 1,3,10 -----	9,18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/01857

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9611245	A	18-04-1996	NONE	
US 3525689	A	25-08-1970	NONE	
US 3833513	A	03-09-1974	NONE	
US 4735146	A	05-04-1988	US 4858534 A	22-08-1989
WO 9612770	A	02-05-1996	US 5714093 A	03-02-1998
			AU 4003695 A	15-05-1996
			CA 2203181 A	02-05-1996
			EP 0788527 A	13-08-1997
DE 4041156	A	25-06-1992	NONE	
WO 9200368	A	09-01-1992	AU 8211191 A	23-01-1992
			CA 2064798 A	23-12-1991
			EP 0535134 A	07-04-1993
			US 5348669 A	20-09-1994
			US 5433872 A	18-07-1995
DE 4423203	A	12-01-1995	JP 7018286 A	20-01-1995
			US 5605957 A	25-02-1997
US 4406800	A	27-09-1983	NONE	
US 4859352	A	22-08-1989	NONE	
WO 9519410	A	20-07-1995	US 5433872 A	18-07-1995
			AU 679829 B	10-07-1997
			AU 1449695 A	01-08-1995
			CA 2181550 A	20-07-1995
			CN 1142244 A	05-02-1997
			EP 0759061 A	26-02-1997
			JP 9508155 T	19-08-1997